Fine and hyperfine structure of the 2p and 3p3πu states of H2

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One- and two-electron fine and hyperfine structure constants of the $2p$ and $3p$ $^3\Pi_u$ levels of the hydrogen molecule have been calculated using the 45–50-configuration elliptic coordinates wavefunctions of Rothenberg and Davidson. The two-electron integrals have been reduced to electron repulsion integrals. The resulting constants agree within 1%–5% with experiment.

I. INTRODUCTION

Recent measurements of the fine structure (fs) and preliminary measurements of the hyperfine structure (hfs) of the $3p$ $^3\Pi_u$ state of H_2 have been made by means of electron induced optically detected magnetic resonance[1,2] and nonzero-field level crossing spectroscopy,[3] both in our laboratory[1,3] and at the Bell Laboratories.[2] This fact, together with the recent publication of the final results[4,5] of older measurements made by metastable beam magnetic resonance of fs and hfs parameters of the analogous $2p$ $^3\Pi_u$ level, lends interest to a calculation of these parameters.

The most important difficulty with this calculation arises from the two-electron fine structure operators for which no method of calculation was, until very recently, available for the molecular case. The only calculations, by Fontana[6] and Chiu[7] used very approximate methods. Fontana used a very crude united-atom wavefunction and Chiu a single-configuration wavefunction and only approximate (10%) solutions of the resultant integrals.

However, a series of papers by Matcha, Kern, and Schrader[8] (MKS) has appeared within the last 3 years. They propose a general method for exact calculation of the two-electron fs integrals using Slater-type orbitals (STO's). However, the better wavefunction now available for the hydrogen $2p$ and $3p$ $^3\Pi_u$ states are not of the STO type, but are the elliptic coordinate 50-configuration wavefunction (without explicit inclusion of r_{12}) of Rothenberg and Davidson[9] (RD). We show that one of the methods used by MKS,[8] namely the reduction of fs integrals to electron repulsion integrals, can be applied to the RD[9] wavefunctions.

The calculation of hfs one-electron integrals is more simple. The first calculation was made by Frey and Mizushima[10] but it was probably in error, as was pointed out by Chiu.[11] Chiu[11] and Jette and Cahill[12] have calculated these integrals using the above-mentioned single-configuration wavefunction of Chiu. More recently Jette used an optimum two-configurations wavefunction.[13]

Sections II and III describe, respectively, the calculation of the two-electron and the one-electron integrals. Section IV deals with the NSO analysis of the wavefunctions, which was made before calculation of the integrals. In Sec. V experimental values are compared with the theoretical results.

II. TWO-ELECTRON INTEGRALS

These are given by the three fine-structure operators,[6,7]

$$B_0=\tfrac{1}{2}\alpha^2(3z_{12}^2-r_{12}^2)/r_{12}^5, \tag{1a}$$

$$B_2=(\tfrac{3}{8})^{1/2}\alpha^2(x_{12}+iy_{12})^2/r_{12}^5 \tag{1b}$$

and

$$A_2=\tfrac{3}{4}\alpha^2[(\mathbf{r}_1-\mathbf{r}_2)\times(\mathbf{p}_2-\mathbf{p}_1)]_z/r_{12}^3. \tag{1c}$$

As pointed out by Schrader,[14] these operators can also be written

$$B_0=-\tfrac{1}{2}\alpha^2\nabla_1^{(0)}\nabla_2^{(0)}(r_{12})^{-1}, \tag{2a}$$

$$B_2=-\alpha^2/6^{1/2}\nabla_1^{(1)}\nabla_2^{(1)}(r_{12})^{-1}, \tag{2b}$$

and

$$A_2=\tfrac{3}{4}\alpha^2\{[\nabla_2^{(1)}(r_{12})^{-1}\nabla_1^{(-1)}-\nabla_2^{(-1)}(r_{12})^{-1}\nabla_1^{(1)}]+[\nabla_1^{(1)}(r_{12})^{-1}\nabla_2^{(-1)}-\nabla_1^{(-1)}(r_{12})^{-1}\nabla_2^{(1)}]\},$$

with

$$\nabla_i^{(0)}=\partial/\partial z_i, \quad \nabla_i^{\pm1}=\pm[(\partial/\partial x_i)\pm i(\partial/\partial y_i)], \quad i=1, 2.$$

The value of A_2 is deduced from Eqs. (3) and (5) of Chiu.[7] Using integration by parts one obtains, for example,

$$\int a(1)b(2)B_0c(1)d(2) = -\tfrac{1}{2}\alpha^2\int(r_{12})^{-1}\nabla_1^{(0)}[a(1)c(1)]\nabla_2^{(0)}[a(2)c(2)] - (4\pi/3)\int a(1)b(1)c(1)d(1), \tag{3}$$

where a, b, c, d are in our case elliptic coordinate basis wavefunctions,

$$|n, j, m, \alpha, \beta\rangle = (2/R)^{3/2}\xi^n\eta^j e^{-\alpha\xi}e^{\beta\eta}[(\xi^2-1)(1-\eta^2)]^{|m|/2}e^{im\phi}/(2\pi)^{1/2}. \tag{4}$$

The last term in (3) gives a net result of zero for triplet wavefunctions and subsequently it is discarded. The usefulness of such a transformation stems from the fact that $\nabla_1^{(\mu)}|n, j, m, \alpha, \beta\rangle$ ($\mu=0, \pm1$) is a linear

combination of a small number of basis functions of the form (4), so that calculation of matrix elements of the operators (1) is reduced to the known calculation of electron repulsion integrals between states of the form (4). This favorable circumstance is analogous to the case of the elliptic basis functions of the Rose gradient formula for the STO used by MKS.[8]

More precisely a straightforward calculation leads to

$$\nabla^{(0)} \mid n, j, m, \alpha, \beta\rangle = [\alpha(\mid n, j+1, m, \alpha, \beta\rangle - \mid n+2, j+1, m, \alpha, \beta\rangle) + \beta(\mid n+1, j, m, \alpha, \beta\rangle - \mid n+1, j+2, m, \alpha, \beta\rangle) + j(\mid n+1, j-1, m, \alpha, \beta\rangle - \mid n+1, j+1, m, \alpha, \beta\rangle) + n(\mid n+1, j+1, m, \alpha, \beta\rangle - \mid n-1, j+1, m, \alpha, \beta\rangle)](2/R)(\xi^2-\eta^2)^{-1}, \quad (5a)$$

$$\nabla^{(1)} \mid n, j, m \geq 0, \alpha, \beta\rangle = (\sqrt{2}/R)(\xi^2-\eta^2)^{-1} \times [\alpha \mid n+1, j, m+1, \alpha, \beta\rangle + \beta \mid n, j+1, m+1, \alpha, \beta\rangle + (j-n) \mid n, j, m+1, \alpha, \beta\rangle] \quad (5b)$$

and

$$\nabla^{(1)} \mid n, j, m<0, \alpha, \beta\rangle = (\sqrt{2}/R)(\xi^2-\eta^2)^{-1}[2m(\mid n+2, j, m+1, \alpha, \beta\rangle - \mid n, j+2, m+1, \alpha, \beta\rangle) + \alpha(\mid n+3, j, m+1, \alpha, \beta\rangle + \mid n+1, j+2, m+1, \alpha, \beta\rangle - \mid n+3, j+2, m+1, \alpha, \beta\rangle - \mid n+1, j, m+1, \alpha, \beta\rangle) + \beta(\mid n+2, j+1, m+1, \alpha, \beta\rangle + \mid n, j+3, m+1, \alpha, \beta\rangle - \mid n+2, j+3, m+1, \alpha, \beta\rangle - \mid n, j+1, m+1, \alpha, \beta\rangle) + (j-n)(\mid n+2, j, m+1, \alpha, \beta\rangle + \mid n, j+2, m+1, \alpha, \beta\rangle - \mid n+2, j+2, m+1, \alpha, \beta\rangle - \mid n, j, m+1, \alpha, \beta\rangle)], \quad (5c)$$

with

$$\nabla^{(-1)} \mid n, j, m, \alpha, \beta\rangle = -[\nabla^{(1)} \mid n, j, m, \alpha, \beta\rangle]^*. \quad (5d)$$

In these calculations, a unique right-handed frame of reference with nuclei A and B located at $-R/2$ and $R/2$ on the z axis, $\xi=(r_A+r_B)/R$ and $\eta=(r_A-r_B)/R$, has been taken.

The term $1/(\xi^2-\eta^2)$ in the formulas (5) is eliminated by the term resulting from the volume differential element

$$dV=(\tfrac{1}{2}R)^3(\xi^2-\eta^2)d\xi d\eta d\phi.$$

A program using the above-mentioned expressions has been written. The resultant $(r_{12})^{-1}$ integrals were computed using a simplified version of the program described by Wahl, Cade, and Roothaan[15] for the exchange integrals upon STO. The simplification stems mainly from the fact that $\beta=0$ in RD wavefunctions. This subroutine has been checked against the tables of Kotani *et al.*[16]

To check the entire program, we have computed the three fs constants B_0, B_2, and A_2 for a pseudo-molecular wavefunction consisting of one configuration of the type

$$\psi=(\tfrac{1}{2})^{1/2}[\psi_{1s}(1)\psi_{2p}(2)-\psi_{1s}(2)\psi_{2p}(1)],$$

with ψ_{1s} and ψ_{2p} normalized STO centered on the middle of the two nuclei and of very large radius $1/\zeta=10^4R$. The value of these constants has been computed directly using formulas 3.1–5 of Chiu.[7] [The power of $2l+1$ is $-\frac{1}{2}$ instead of $+\frac{1}{2}$ as misprinted in Eq. (3.4) of Chiu.[7]] These values have been compared with the result of our program which used for ψ_{1s} and ψ_{2p}, the approximations

$$\psi_{1s}=(\tfrac{1}{2}\zeta R)^{3/2} \mid 0, 0, 0, \tfrac{1}{2}\zeta R, 0\rangle$$

and

$$\psi_{2p}=-(\zeta R)^{5/2}/4\sqrt{2} \mid 0, 0, 1, \tfrac{1}{2}\zeta R, 0\rangle,$$

which tend asymptotically to the correct Slater wavefunctions when $\zeta\to 0$. The two calculations, based on two entirely different methods give the same result to within at least six significant figures.

III. ONE-ELECTRON OPERATORS

We have the spin–orbit,

$$A_1=\alpha^2/4 \sum_{i=1,2,n=1,2} l_{iz}/r_{in}^3, \quad (6a)$$

and hfs operators (with the normalization of Refs. 4, 12, and 13),

$$a=g_I A_1, \quad (6b)$$

$$a_F=\tfrac{1}{3}\pi g_I\alpha^2 \sum_{i,n} \delta((r_{in}), \quad (6c)$$

$$c=(3/16)g_I\alpha^2 \sum_{i,n} (3z_{in}^2-r_{in}^2)/r_{in}^5, \quad (6d)$$

and

$$d=(3/16)g_I\alpha^2 \sum_{i,n} (x_{in}+iy_{in})^2/r_{in}^5, \quad (6e)$$

where i is the ith electron and n the nth nucleus.

The resulting integrals have been computed numerically using crossed Gaussian integration. A similar procedure was used for fs one-electron operators by Matcha, Kouri, and Kern,[17] who reduced their STO wavefunctions to elliptic form in the case of hybrid integrals. The only problem came from the c integrals which diverge if one uses this method directly. The

TABLE I. fs and hfs constants as a function of internuclear distance.

R (a.u.)	B_0 (MHz)	B_2 (MHz)	A_1 (MHz)	A_2 (MHz)	A (MHz)	a (MHz)	a_F (MHz)	c (MHz)	d (MHz)
				$2p\,^3\Pi_u$					
0[a]	−2392	−5859	7300	−12 557	−5257	22.21	5684	−6.66[d]	−13.32
0[b]	−2911	−7131			−5513				
1.90	−1726	−4841	8698	−13 049	−4351	26.46	466.9	60.47	−16.12
1.95	−1680	−4713	8532	−12 807	−4275	25.95	455.1	57.54	−15.81
2.00	−1635	−4645	8368	−12 565	−4197	25.45	443.9	54.89	−15.50
2.05	−1590	−4551	8205	−12 325	−4120	24.96	433.5	52.33	−15.19
2.10	−1546	−4457	8044	−12 086	−4042	24.47	423.6	49.93	−14.89
∞[c]	0	0	3650	0	3650	12.10	355	−3.33[d]	−6.66
				$3p\,^3\Pi_u$					
0[a]	−682	−1673	2163	−3 744	−1581	6.58	5684	−1.97[d]	−3.95
0[b]	−792	−1939			−1516		5684		
1.90	−416	−1159	2062	−3 151	−1089	6.27	480.9	69.26	−3.84
1.95	−405	−1133	2011	−3 078	−1067	6.12	469.1	66.14	−3.74
2.00	−394	−1107	1962	−3 008	−1046	5.97	458.0	63.22	−3.66
2.05	−383	−1083	1915	−2 939	−1024	5.83	447.5	60.46	−3.57
2.10	−373	−1058	1870	−2 873	−1003	5.69	437.8	57.85	−3.49
∞[c]	0	0	1081	0	1081	3.29	355	−0.99[d]	−1.97

[a] Rough calculation using a wavefunction consisting of $1s(Z=2)$ and $np(Z=1)$ electrons.

[b] Deduced from experimentally measured[18,19] separations of fs or hfs levels in He using $E_0-E_2=-3A-\frac{9}{2}B_0$, $E_1-E_2=-2A+3B_0$, and $B_2=6^{1/2}B_0$.

[c] Separation of the H_2 molecule into the one $1s$ and one $1p$ electron.

[d] This curious result is due to the fact that in both ($R=0$ and $R=\infty$) limits, the $1s$ electron gives no contribution to c, for symmetry reasons, whereas the σ orbital, by means of its "p, $d\cdots$components" gives a contribution much larger than, and of the opposite sign from, the outer $n\Pi$ orbital, because it is much closer to the two nuclei.

problem is as follows. The various one-electron operators are of the form $N(\xi,\eta)/r_B^3$ (or r_A^3), where $N(\xi,\eta)$, the numerator, depends on the particular operator. Such an operator, when integrated between two basis functions (4) yields integrals of the form

$$\left(\frac{2}{R}\right)^3\int_{-1}^{+1}d\eta\int_1^\infty d\xi\,\exp[-(\alpha_1+\alpha_2)\xi]\xi^{n_1+n_2}\eta^{j_1+j_2}$$

$$\times[(\xi^2-1)(1-\eta^2)]^{(|m_1|+|m_2|)/2}N(\xi,\eta)\frac{\xi+\eta}{(\xi-\eta)^2}, \quad (7)$$

with $\beta=0$ in the RD wavefunctions.

The term $1/(\xi-\eta)^2$ diverges when $\xi\to1$ and $\eta\to1$ and must be compensated for by a numerator vanishing in the same limit:

For a and A_1, the l_{1z} operator eliminates terms for which $\frac{1}{2}(|m_1|+|m_2|)<1$. When $\xi=1+\epsilon$, $\eta=1-\epsilon'$, the integrand is then of the order $(\xi^2-1)(1-\eta^2)/(\xi-\eta)^2=\epsilon\epsilon'/(\epsilon+\epsilon')^2$. This quantity, though singular near $\epsilon=\epsilon'=0$, is always finite and the corresponding integrals converge without difficulty.

For d, two factors $(\xi^2-1)(1-\eta^2)$ come from $N(\xi,\eta)$ and from $[(\xi^2-1)(1-\eta^2)]^{(|m_1|+|m_2|)/2}$.

For c, there is nothing analogous. The numerator $N(\xi,\eta)=3(1-\xi\eta)^2/(\xi-\eta)^2-1$ does not tend to zero when ξ and η tend to 1, and no symmetry argument precludes the case $|m_1|=|m_2|=0$ (the matrix element between two σ charge distributions is nonzero). The origin of this divergence can be traced to the following fact. The matrix element of c_B (the part of c centered on the nucleus B) is proportional to

$$\int_0^\infty \exp[-(\zeta_1+\zeta_2)r]\frac{r^{n_1-1}r^{n_2-1}}{r^3}r^2dr$$

$$\times\int Y_{l_1}^{m_1*}(\Omega)\,Y_2^0(\Omega)\,Y_{l_2}^{m_2}(\Omega)\,d\Omega. \quad (8)$$

For two $1s$ orbitals, $n_1=n_2=1$, $l_1=l_2=m_1=m_2=0$, the radial integral diverges near $r=0$, while the angular integral is always zero, due to the triangle rule imposed upon l_1, l_2, and 2. Then, if we integrate, as usual, first on a sphere centered upon B, and only after along the radius, the result is zero. But, when we use elliptic coordinates, we integrate along ellipsoids of hyperboloids of foci A and B, so that the integral diverges. To solve this problem, we have then subtracted, from the integral (7) when $|m_1|=|m_2|=0$, its "$1s$

TABLE II. fs and hfs constants. Comparison between theory and experiment.

	$2p\ ^3\Pi_u$				$3p\ ^3\Pi_u$	
Constant	Exptl[4]	Chiu[7,11]	Jette[13]	This work	Exptl[1-3]	This work
a_F	450.479	545	471.14	449.7		458.6
a	26.6[a]	17.44	21.98	25.6		5.96
c		44.72	59.37	56.3		63.3
d		−10.13	−12.87	−15.6		−3.65
$c-3d$	104.177	75.11	97.98	103.1		74.2
B_0	−1 420.807[b]	−1 330		−1 651		−393
B_2	−4 483.911[b]	−3 840		−4 681		−1105
$6^{1/2}B_2-B_0$	−9 562.488	−8 100		−9 815	−2143	−2314
$6^{1/2}B_2+B_0$	−12 404.10[b]	−10 800		−13 117[c]	−2987[d]	−3100
				−12 875[e]		
A_1	8 750[f]	+5 737		+8 424		1960
A_2	−12 467[g]	−9 800		−12 644		−3003
$A=A_1+A_2$	−3 717.120	−4 100		−4 220	−736	−1043

[a] Low precision measurements (±0.5 MHz).
[b] Doubtful results due to the fact that the vibrational level for which $6^{1/2}B_2+B_0$ is measured is uncertain (either 0 or 1).
[c] $v=0$.
[d] Deduced from the results of Ref. 1 which give $A-(3/10)(B_0+6^{1/2}B_2)$.
[e] $v=1$.
[f] Low precision result (±2%). Deduced from multiplication of a by g_I.
[g] d^0: deduced from a and A.

component," i.e., the integral

$$\exp[-(\alpha_1+\alpha_2)]\left(\frac{2}{R}\right)^3\int_{-1}^{+1}d\eta\int_1^\infty d\xi \times\exp[-(\alpha_1+\alpha_2)(\xi-\eta)]\frac{\xi+\eta}{(\xi-\eta)^2}Nc_B(\xi,\eta)d\xi d\eta = \exp[-(\alpha_1+\alpha_2)]\left(\frac{2}{R}\right)^3\int_0^\infty \exp[-(\alpha_1+\alpha_2)r_B]\times\frac{dr_B}{r_B}\int_{-1}^{+1}d(\cos\theta_B)(3\cos^2\theta_B-1), \quad (9)$$

which is identically zero according to the above discussion. The $\exp[-(\alpha_1+\alpha_2)]$ term in front has been added so that the two exponential factors in (7) and (9) become equal when $\eta\to1$. In (ξ,η) coordinates, the integrand, when $\xi=1+\epsilon$ and $\eta=1-\epsilon'$, is of the order $\exp[-(\alpha_1+\alpha_2)][(n_1+n_2)\epsilon+(j_1+j_2)\epsilon']/(\epsilon+\epsilon')^2$. This quantity goes to infinity when both ϵ and ϵ' tend to zero, but the corresponding integral converges, very slowly however. To have a rapid convergence, the integration variables $\cos\theta_B$ and r_B, or rather $t_B=(1-r_B)/(1+r_B)$ have been used in order to have the $[-1, +1]$ integration interval needed for Gaussian integration. In this case the $1/r_B$ divergent term on the rhs of (9) is compensated for by the fact the two integrands in (7) and on the rhs of (9) become equal when $r_B\to0$, so that the integrand is always finite and the integral is rapidly convergent. Double precision arithmetic has been used on an IBM 360 throughout to avoid rounding errors which would be very important in such a substraction procedure.

IV. NSO ANALYSIS

It has been shown by Rothenberg and Davidson[9] that for the excited levels of hydrogen the convergence of the natural spin orbital (NSO) development is extremely rapid. The first NSO has a weight of more than 99%. Thus, instead of the RD wavefunctions in the original wavefunction form,

$$\psi(r_1,r_2)=\sum_{i,j}c_{ij}\tfrac{1}{2}[\phi_i(1)\phi_j(2)-\phi_i(2)\phi_j(1)] \quad (10)$$

with ϕ_i the basis functions in elliptical coordinates (4), we use the NSO wavefunctions,

$$\psi(r_1,r_2)=\sum_i(\sqrt{2}a_i)\times(\sqrt{2})^{-1}[f_i^*(1)g_i(2)-f_i^*(2)g_i(1)],$$

with

$$f_i(1)=\sum_k f_{ik}\phi_k(1) \quad\text{and}\quad g_i(2)=\sum_k g_{ik}\phi_k(2).$$

The NSO analysis has been made, for the five interatomic distances for which RD calculated the wavefunctions, by the method described in Ref. 9. For $R=2.0$ the results agree with those of RD [9] except for some least significant figures. It has been checked on

TABLE III. fs and hfs constants of the $2p$ $^3\Pi_u$ level as a function of the number of NSO included.

Constant	First NSO	$\sigma_g\Pi_u$	$\sigma_u\Pi_g$	$\Pi_u\delta_g$	$\Pi_g\delta_u$	$\delta_g\Phi_u$	Exptl
B_0	−2 057	−1 948	−1 706	−1 662	−1 653	−1 651	
B_2	−5 560	−5 269	−4 931	−4 714	−4 695	−4 681	
$6^{1/2}B_2-B_0$	−11 562	−10 958	−10 372	−9 885	−9 847	−9 815	−9 562.488
$6^{1/2}B_2-B_0$ [a]	−15 411	−14 618	−13 532	−12 965	−12 910	−12 875	−12 404.10
A_2	−15 012	−14 501	−13 686	−12 765	−12 702	−12 645	
A_1	8 366	8 415	8 458	8 426	8 425	8 424	
A	−6 646	−6 086	−5 228	−4 339	−4 277	−4 221	−3 717.120
a_F	448.32	448.66	449.74	449.74	449.74	449.74	450.479
c	56.29	56.37	56.33	56.30	56.30	56.30	
d	−14.70	−14.78	−14.86	−15.63	−15.61	−15.61	
$c-3d$	100.39	100.70	100.91	103.18	103.12	103.12	104.177

[a] $v=1$. All other results are for $v=0$.

a particular $\xi\eta$ term that the NSO wavefunctions and the configuration wavefunction agree to within all eight significant figures.

In the calculation of the various fs and hfs constants, the minor NSO have a contribution coming mainly from their cross term with the first NSO, of weight $2\times(\sqrt{2}a_i)\times(\sqrt{2}a_1)$. To take this into account, all the NSO (13 for the $3p$ $^3\Pi_u$ and 15 for the $2p$ $^3\Pi_u$) have been included, and a cutoff of 0.75×10^{-4} for the two-electron and 10^{-6} for the one-electron, faster to compute, operators, has been taken on the weight $(\sqrt{2}a_i\times\sqrt{2}a_j)$ of the various terms. For the two-electron operators, it has been checked in one particular case that choosing a cutoff of 10^{-5} would double the computation time and modify the results by only 0.1%. Taking into account only the NSO given by Ref. 9 would result in an error of 2%. For the case of the one-electron operators the orthonormality of the NSO preclude, except for the exchange contribution to the d coefficient, any cross term between NSO so that the convergence is very rapid and the cutoff can be set much lower. The difference between a test calculation of A_1 made with the full original configuration form wavefunctions and another made with NSO wavefunctions and a cutoff of 10^{-6} is of the order of 10^{-8}.

V. RESULTS AND DISCUSSION

The results of the calculations for the five interatomic distances for which RD have calculated their wavefunctions is given in Table I. To average over the vibrational wavefunction, we have used the following procedure.[20] The potential is expanded in the form

$$V=\tfrac{1}{2}\omega_e q^2+k_1q^3, \tag{11}$$

where $q=(R-R_e)/\epsilon$ with $\epsilon=(\hbar/\mu\omega_e)^{1/2}$. The coefficients ω_e and k_1 are deduced from the spectroscopic data of Herzberg.[21] The coefficient P is then expanded in a power series,

$$P=P_0+\alpha q+\beta q^2. \tag{12}$$

Then, it can be shown,[20] using perturbation theory, that

$$P=P_0+[\beta-(3k_1\alpha/\omega_e)][v+\tfrac{1}{2}]. \tag{13}$$

The main drawback with this procedure is due to the fact that the five interatomic distances used are all very near the minimum of the interatomic potential, corresponding to only one-third of the distance between classical turning points for the zeroth vibrational level, and one-tenth for the third vibrational level. The formula (12) is then probably good for the zeroth vibrational level, but may be rather poor for the third or fourth vibrational level. To illustrate this fact, we have given, in Table I, the values of various constants for $R=0$ and $R=\infty$. This is of little importance for the results presented in this paper, which are mainly for $v=0$, and for which we expect an accuracy of better than 1%, but one must be careful in applying these formulas to the higher vibrational levels of $3p$ $^3\Pi_u$ for which measurements have been reported,[1,3] and for which further measurements are projected.[2]

The final results are given in Table II. We see that the one-electron constants are good to better than 1%, in much better agreement with experiment than the previous calculations. The individual two-electron constants are good to within 2%–4%, systematically larger than the experiment, whereas Chiu's values are approximately 15% lower. The A and B coefficients for the $2p$ $^3\Pi_u$ level need separate discussions.

$6^{1/2}B_2-B_0$ has been certainly measured for $v=0$, whereas $6^{1/2}B_2+B_0$ can have been measured either for $v=0$ or $v=1$.[4] Our results favor the second hypothesis. In this latter case, only these linear combinations make sense and are to be compared with our calculations, and the "measured" values of B_0 and B_2 are incorrect.

Measurements give directly only $A=A_1+A_2$, but not separately A_1 and A_2. However, the fact that $a=g_I A_1$ has been used to give an "experimental" value of A_1 deduced from the measured a, and then for A_2. These "experimental" values of A_1 and A_2 are of a somewhat low precision because the a coefficient is only accurate to $\pm 2\%$.[4] Nevertheless, we see that our individual A coefficients are good to within 1%–4% whereas Chiu's have 20%–35% accuracy. We then see that the fact that the final result of Chiu for $A=A_1+A_2$ is better than for our calculation is only a matter of chance, since the result is the difference of two incorrect results.

Table II shows that, while the computed accuracy of one-electron coefficients is good, it is several times lower for two-electron coefficients, and consequently is insufficient, mostly because certain measured coefficients (A and particularly the results of Refs. 1 and 3) are given in terms of differences of much larger coefficients. To study the origin of this difference in accuracy, Table III gives the variation of the various coefficients as a function of the number of NSO included, classifying them according to their symmetry. We see that the one-electron coefficients have apparently converged, the influence of the NSO other than the first one (i.e., of correlation) being quite unimportant.

Better results for these coefficients can then be obtained mainly by improving the accuracy of the first NSO (by better nonlinear parameter adjustment or by including higher powers in ξ and η), or of the vibrational averaging, the difference between theory and experiment being not too far from what is expected to be due to various higher-order interactions.[5]

For the two-electron operators, as was to be expected, the influence of correlation is much bigger, decreasing the coefficients by some 20%, the convergence is much slower, so that, if the discrepancy is not due to insufficient accuracy of the first NSO, a great number of additional NSO has to be included in order to obtain the desirable 1% level of accuracy. It is not surprising that the RD wavefunction, having no r_{12} term, cannot give with enough accuracy the short-range repulsion which is essential in $1/r_{12}^3$ operators. Therefore, it would be necessary, in order to increase significantly the accuracy, to use wavefunctions analogous to those that Kolos and Wolniewicz[22] have computed for other levels of H_2.

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